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Supporting Information for

Characterization of Laser-Induced Breakdown Spectroscopy (LIBS) emission lines for the identification of chlorides, carbonates, and sulfates in salt/basalt mixtures for the application to MSL ChemCam data

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Contents of this file

Additional Supporting Information (Files uploaded separately)

Text files of raw data for 69 samples
CSV files of "minimally-processed" data for 69 samples
Text file of calibration curve values

Introduction

Additional information regarding the prepared mixtures and the full set of spectra and calibration curves for Cl and C lines selected for analysis are provided here. The grain size distributions of an example basalt and salt used in the mixtures are shown in Figure S1. The results of the independent chemical analysis performed by Activation Laboratories Ltd. are included in Table S1 and a comparison with the expected values is shown in Figure S2. The identification labels for mixtures from this work included as supplementary data and the subset included in *Clegg et al.* [2017] are given in Table S2. Figures S3 and S4 provide spectra over the range of salt concentrations for each mixture combination and the corresponding calibration curves for the 16 Cl lines and 7 C lines analyzed in this work. See the main text for more details. Figure S5 shows

the CaCl molecular line regions for the chloride+basalt compositional series in this work. Also included (as separate files) are the data collected from the instrument prior to processing and the "minimally-processed" data as described in section 2.2 of the main text. Finally, a text file is included containing the peak area values shown in Figures 5, S3 and S4.

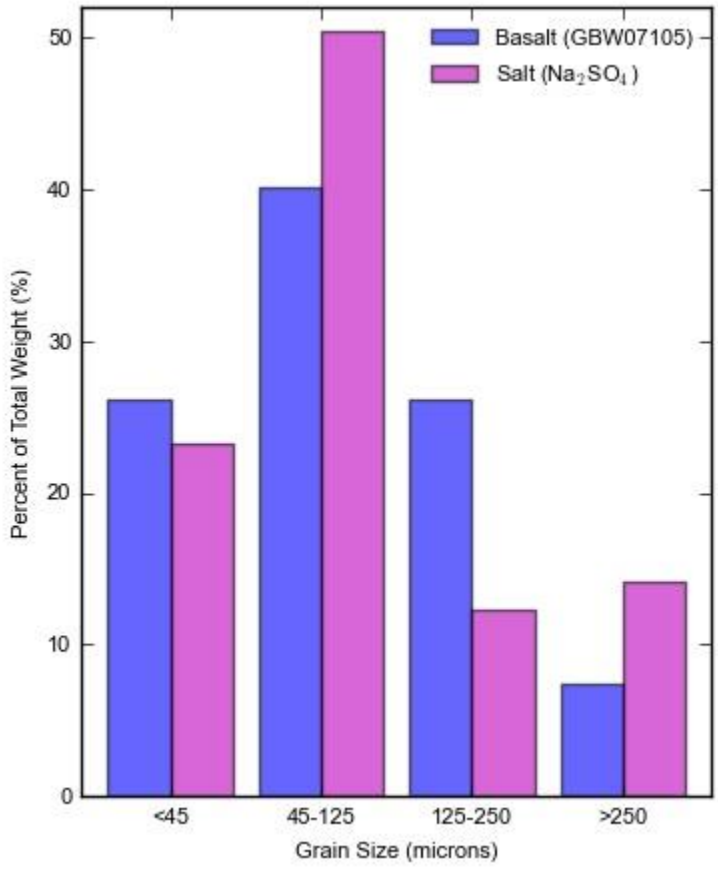


Figure S1. Histogram of grain sizes in GBW07105 (basalt) and Na_2SO_4 used in mixtures. Results based on dry sieving 18g of powder that had been pulverized for several minutes in a shatterbox.

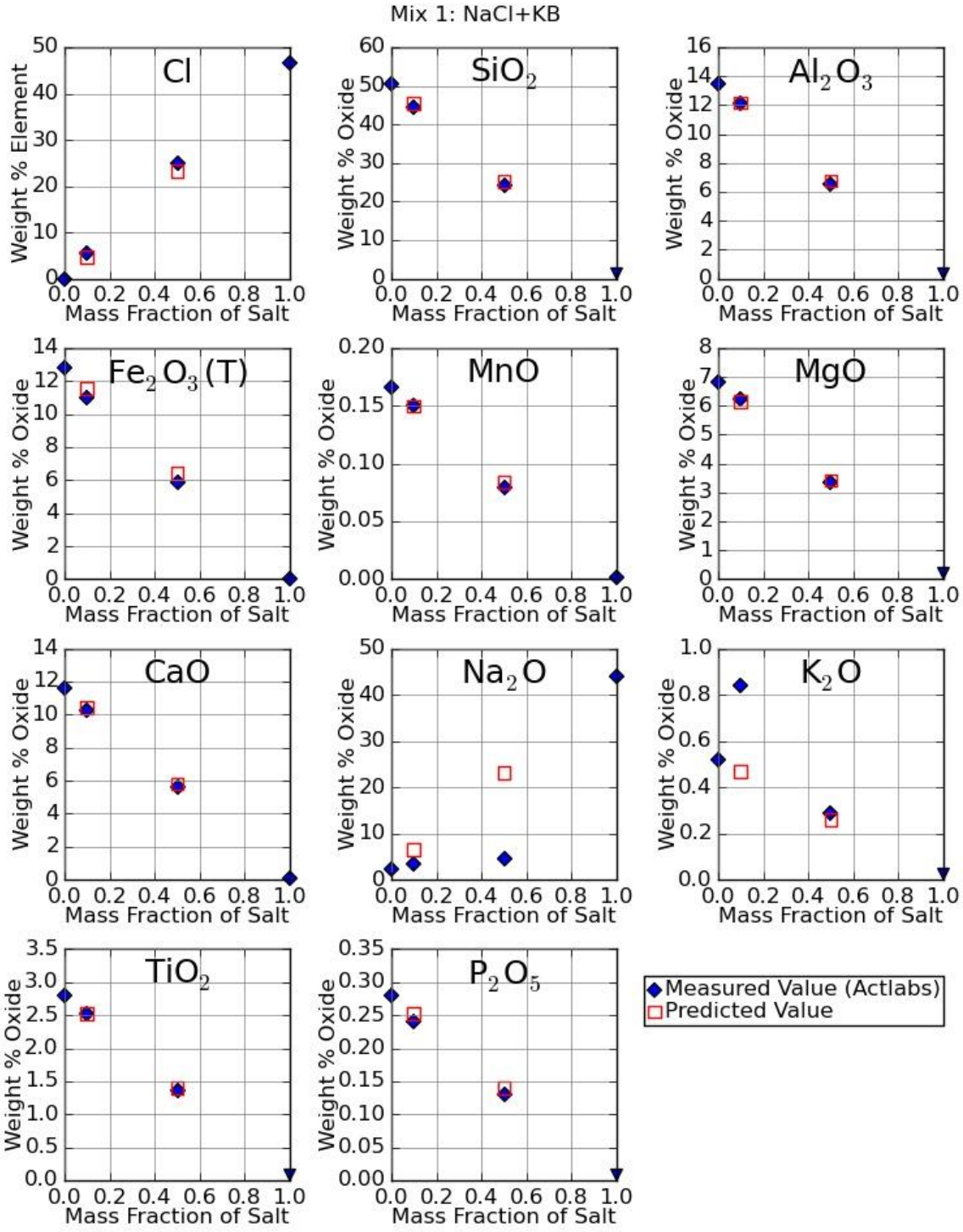


Figure S2. Comparison of elemental compositions determined by Actlabs to expected mixture compositions. Note that where discrepancies occur (for Na, K, P; not examined for this study) we suggest that the expected value is more likely to be the true mixture value because of the correspondence for other elements and known challenges in measuring somewhat volatile phases.

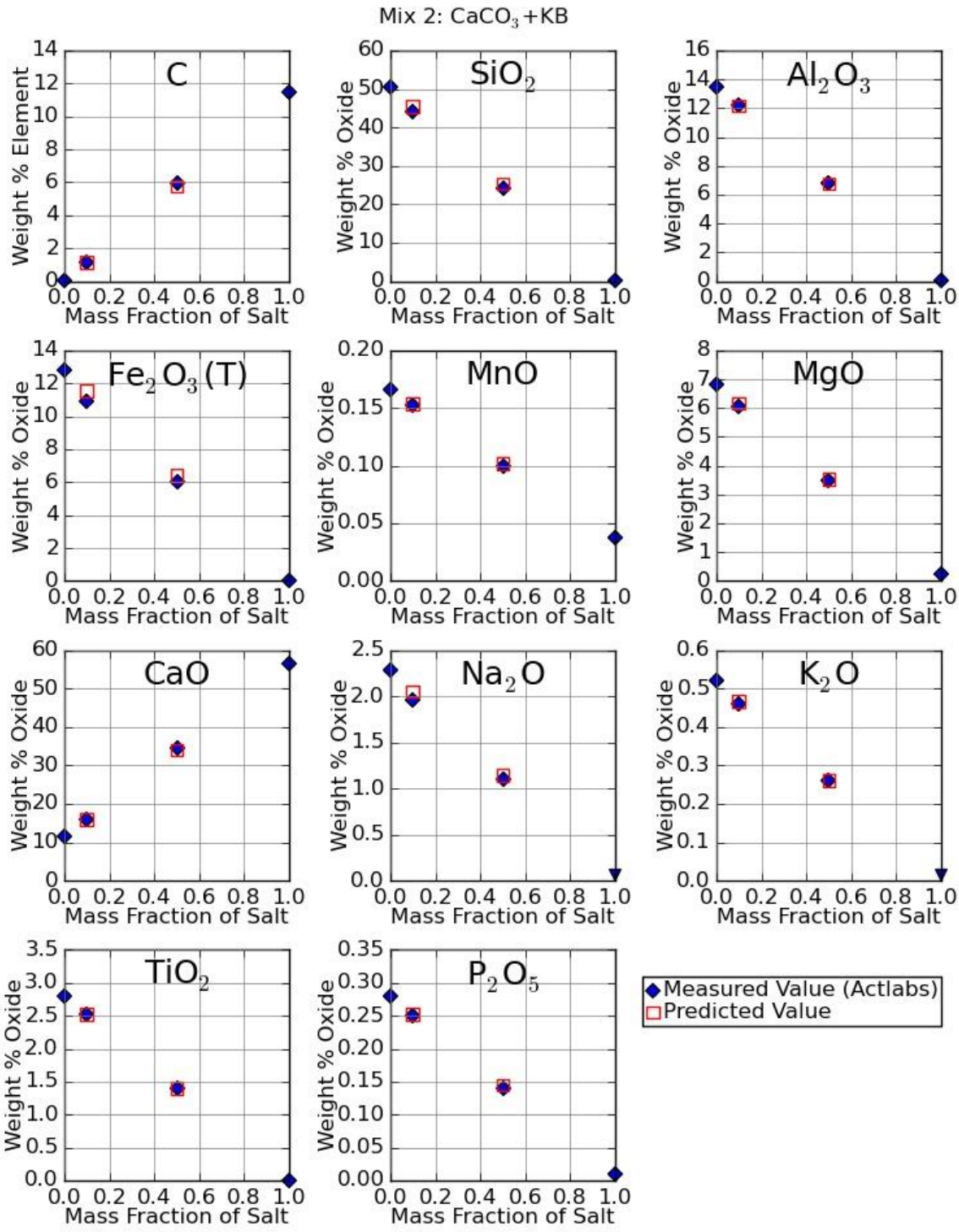
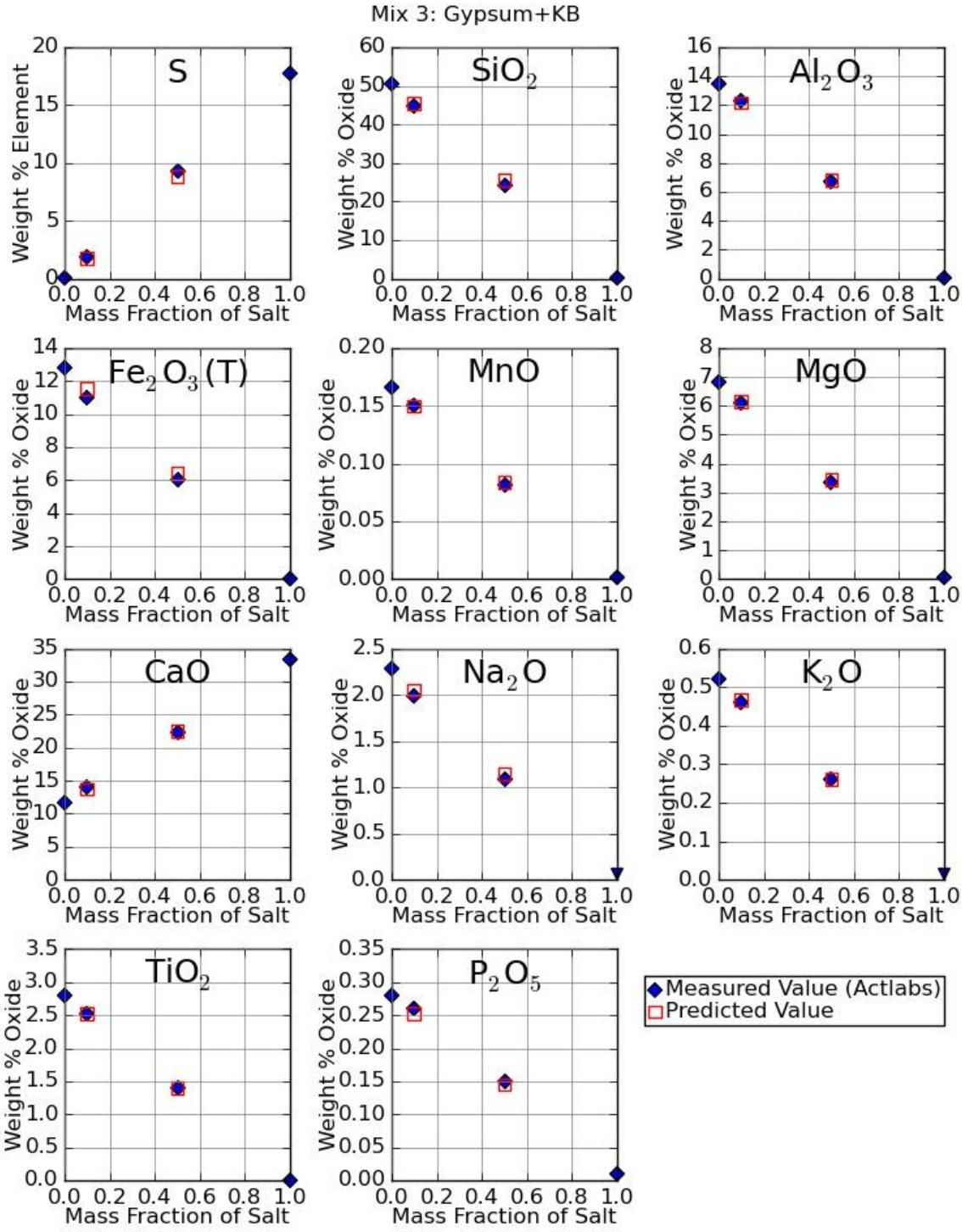


Figure S2. Continued.



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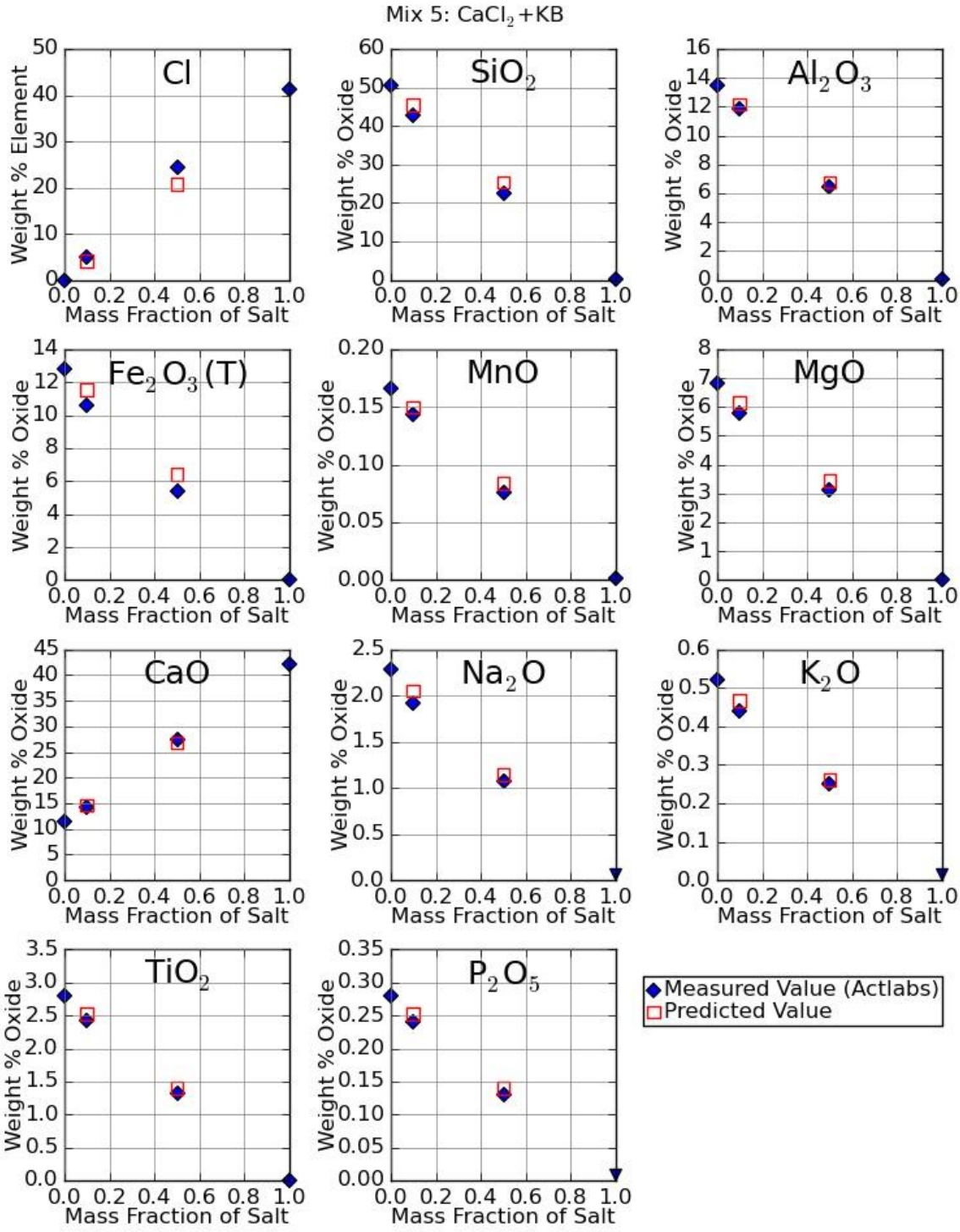

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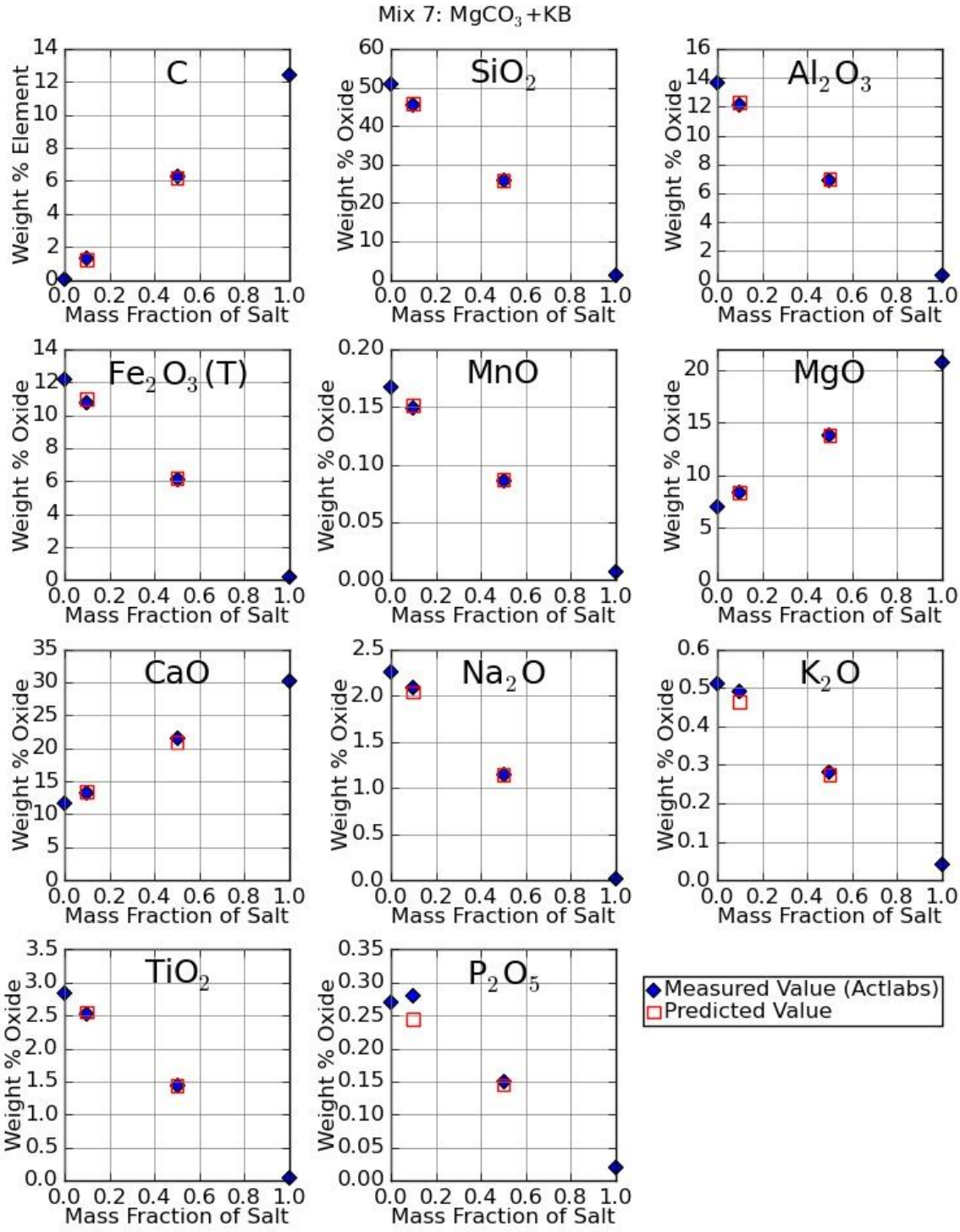

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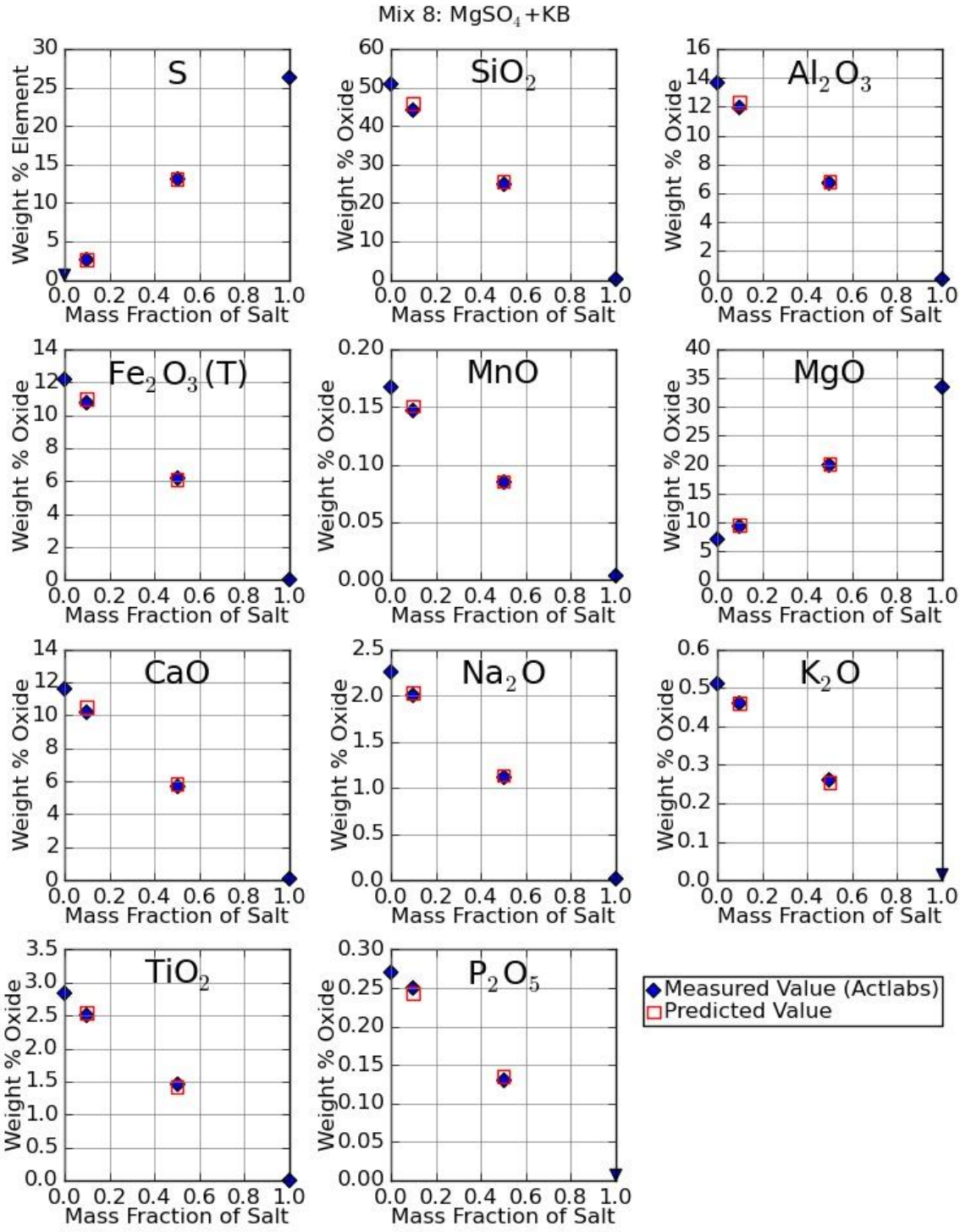

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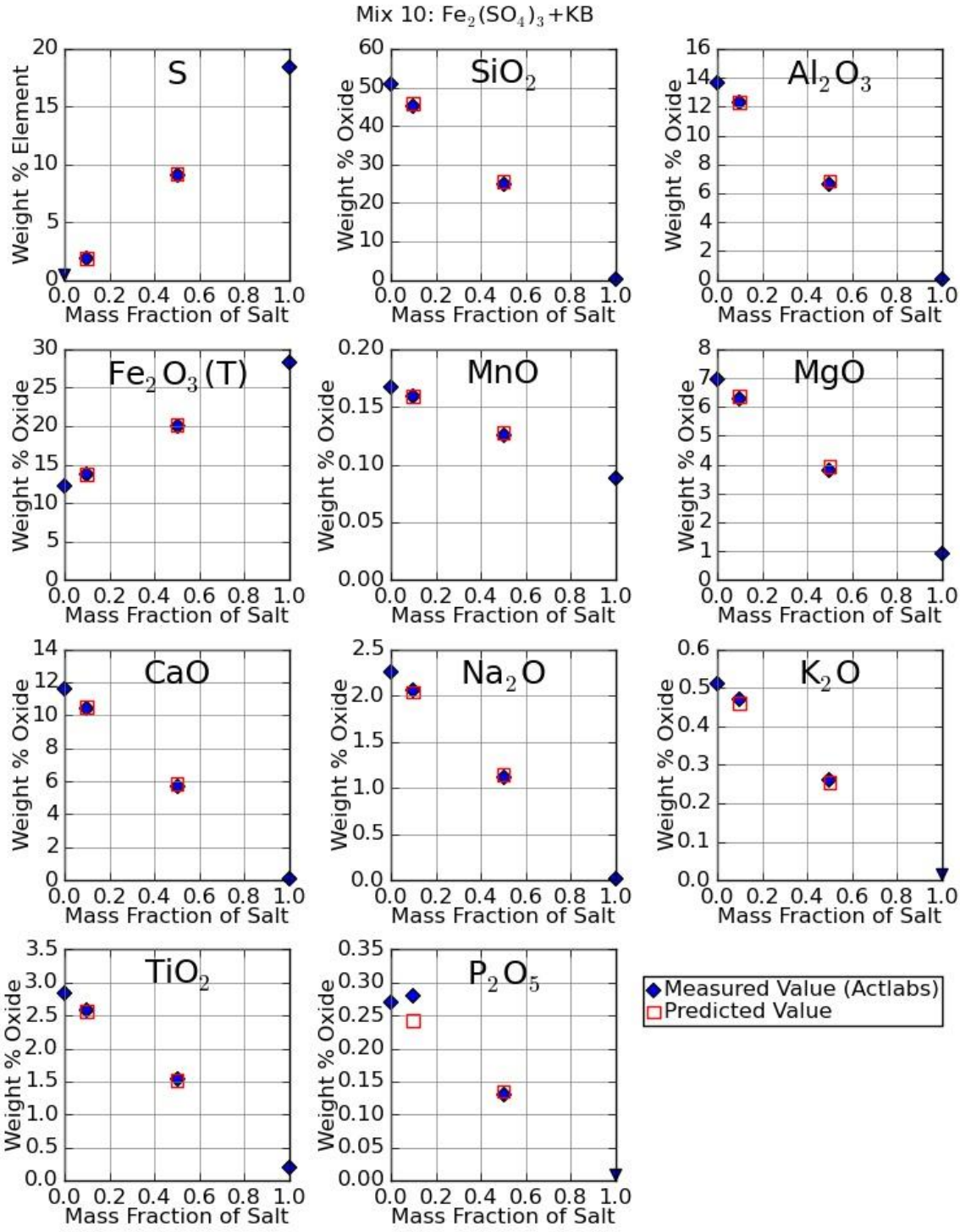

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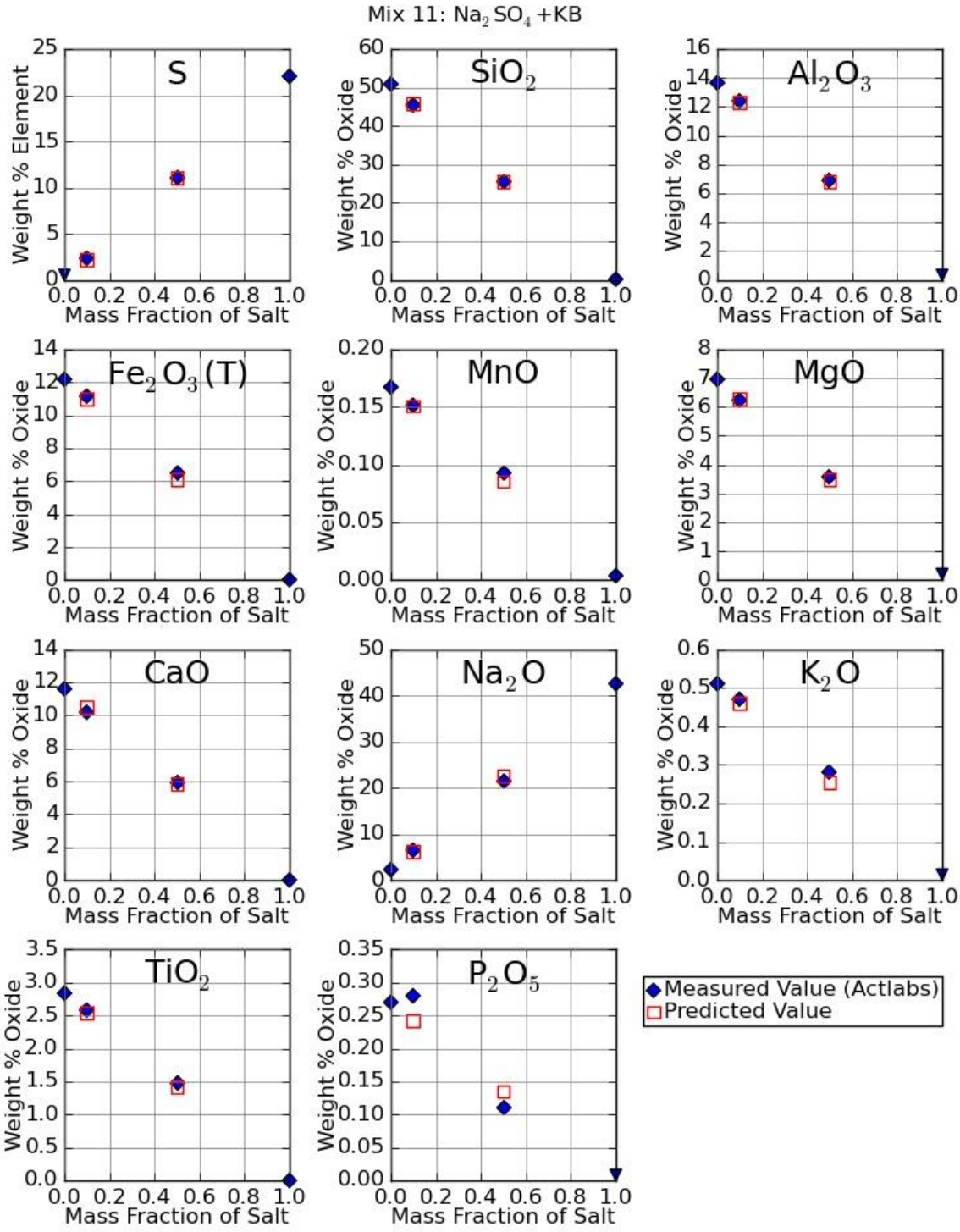

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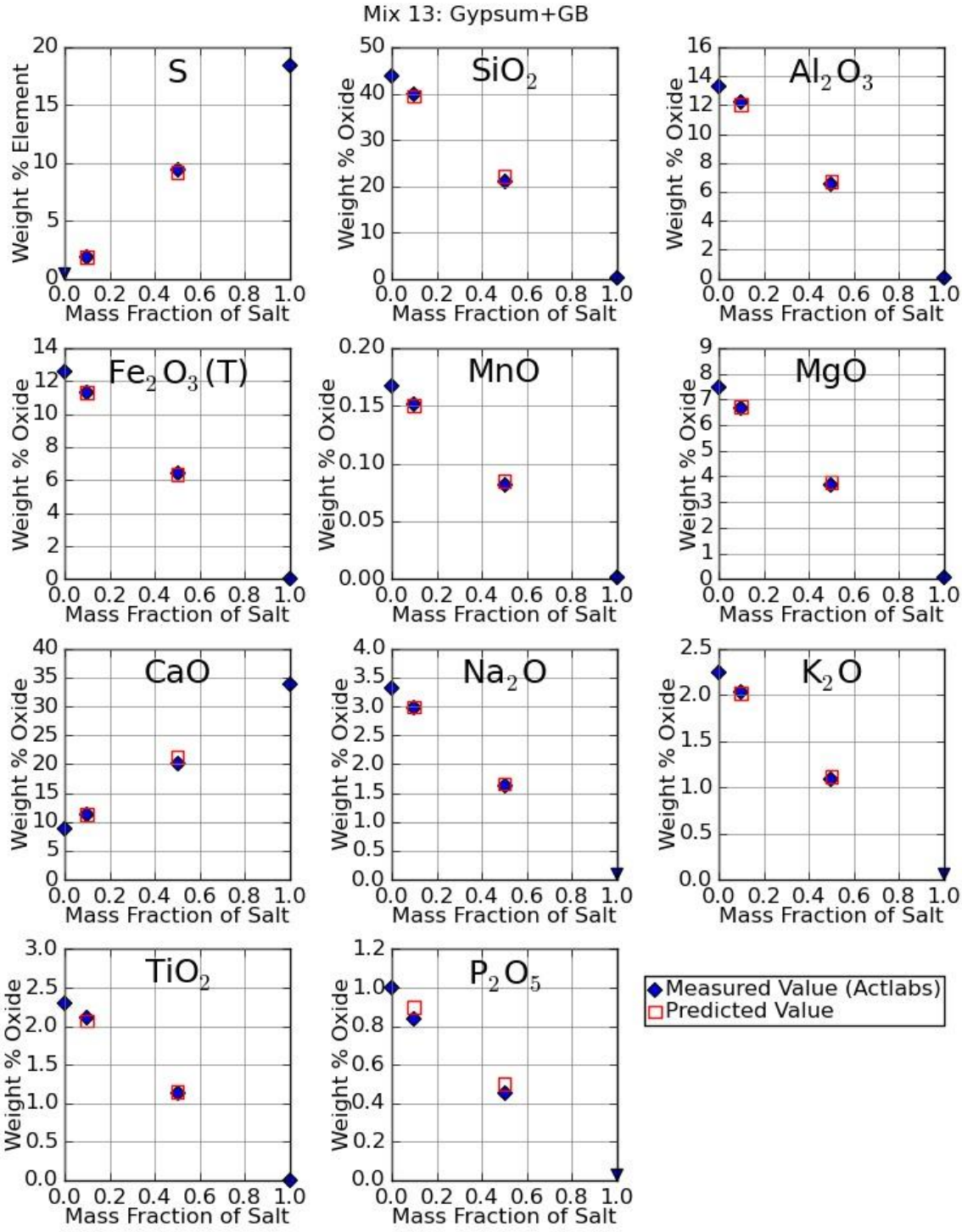

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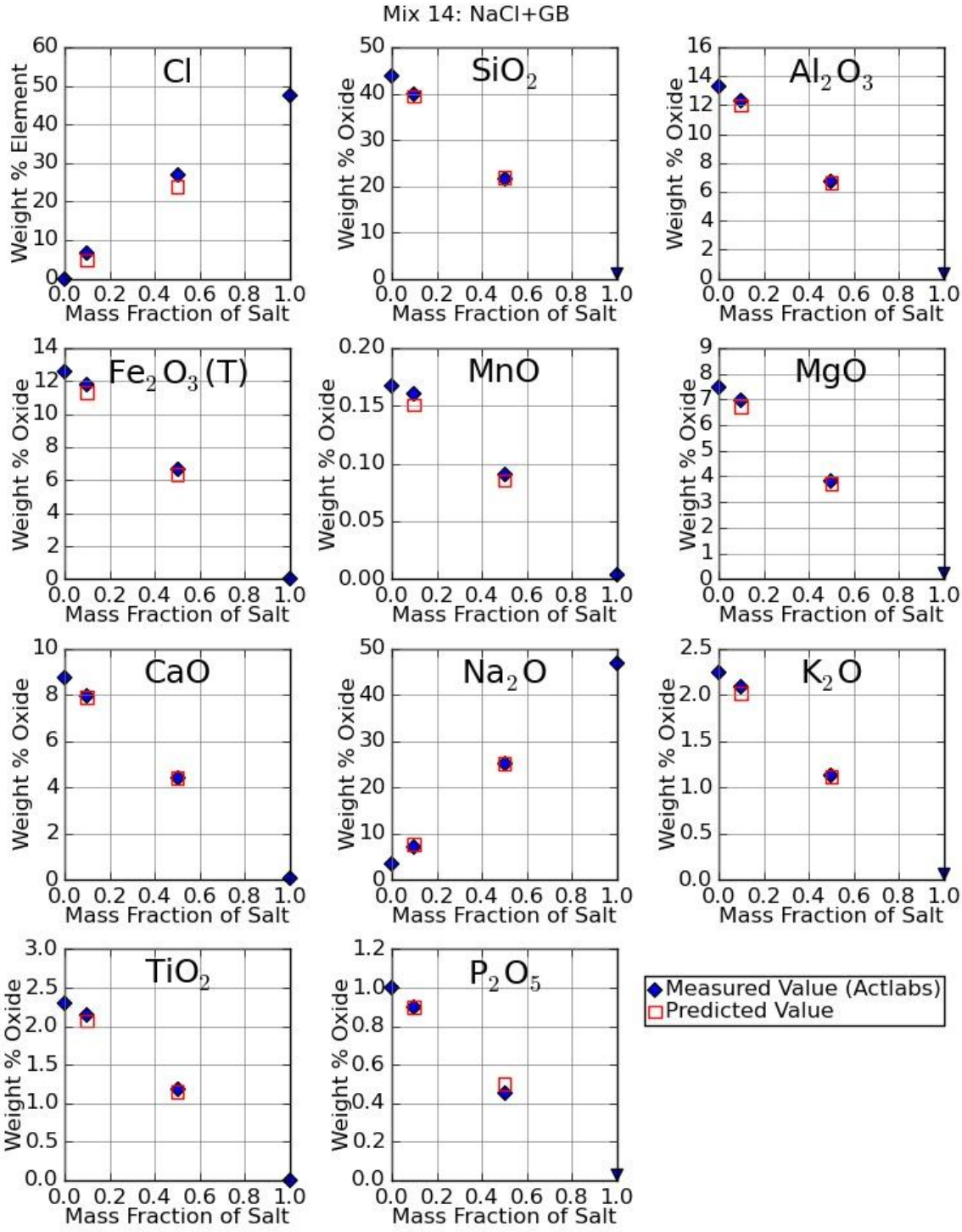

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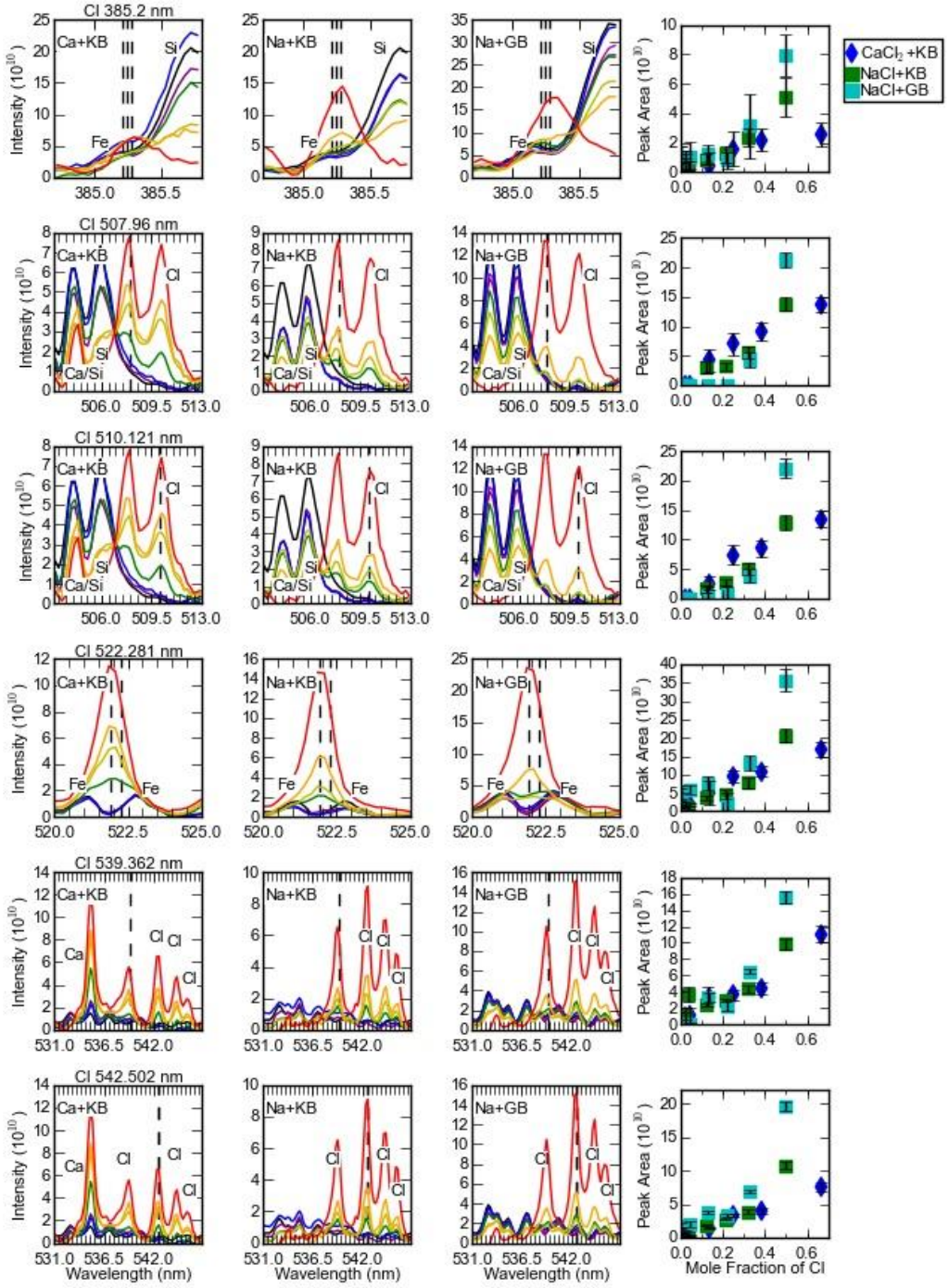

Figure S3. Spectra of Cl emission lines (denoted by vertical lines) in NaCl+K1919 (Na+KB), $CaCl_2$+K1919 (Ca+KB), and NaCl+GBW07105 (Na+GB) mixtures. Colors in the overlain spectra indicate different salt concentrations with pure basalt in black, pure salt in red, and mixtures containing salt mass fractions of 0.05 wt. % (select mixtures only) in magenta, 5 wt. % in purple, 10 wt. % in blue, 30 wt. % in green, 50 wt. % in yellow, and 70 wt. % in orange. Intensity is in units of photons/shot/mm^2/sr/nm. Calibration curves for the corresponding Cl peaks in NaCl+K1919 (green squares), $CaCl_2$+K1919 (blue diamonds), and NaCl+GBW (cyan squares) are shown in the rightmost panel. Peak areas are in units of photons/shot/mm^2/sr.

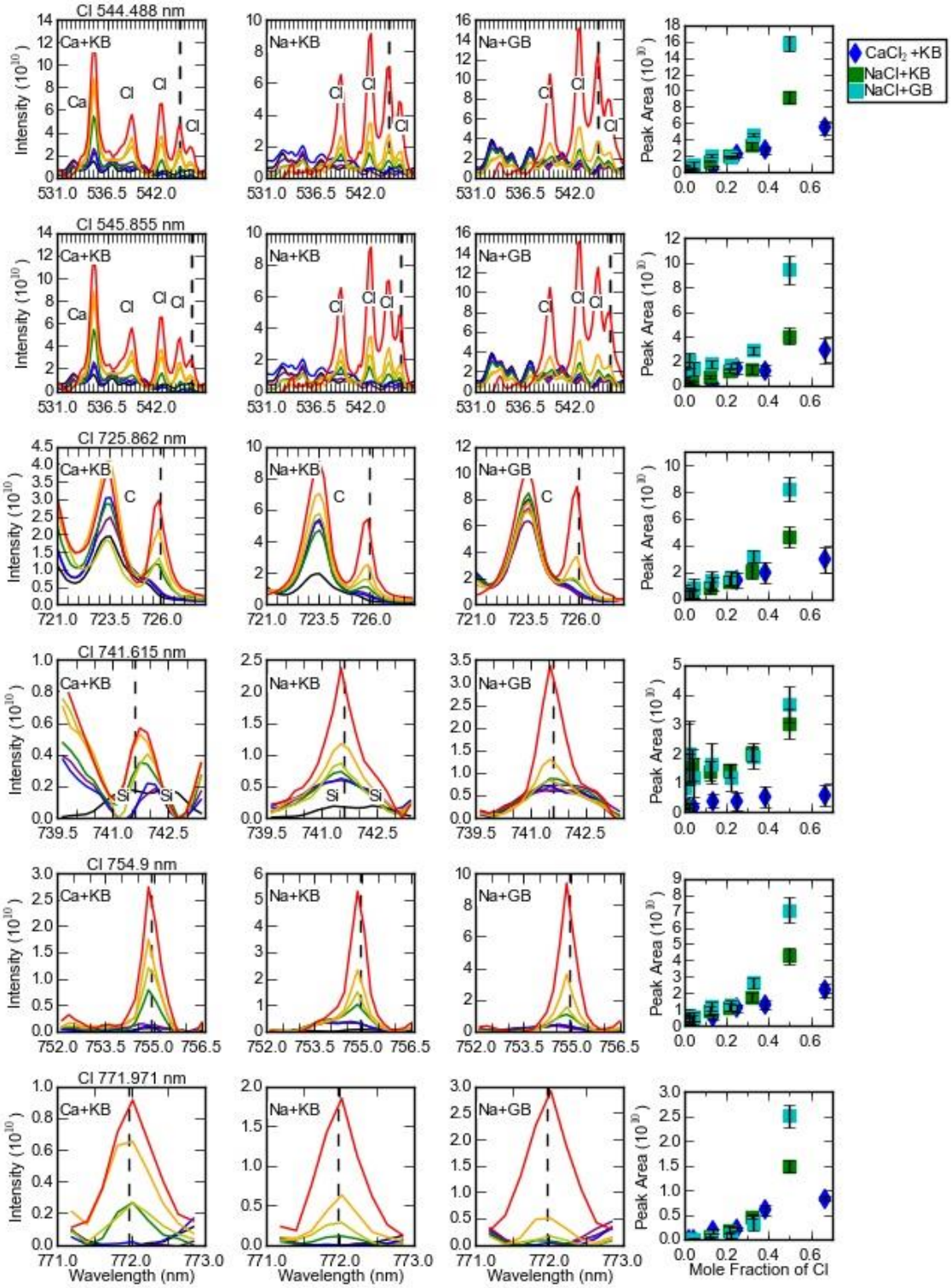

Figure S3. Continued

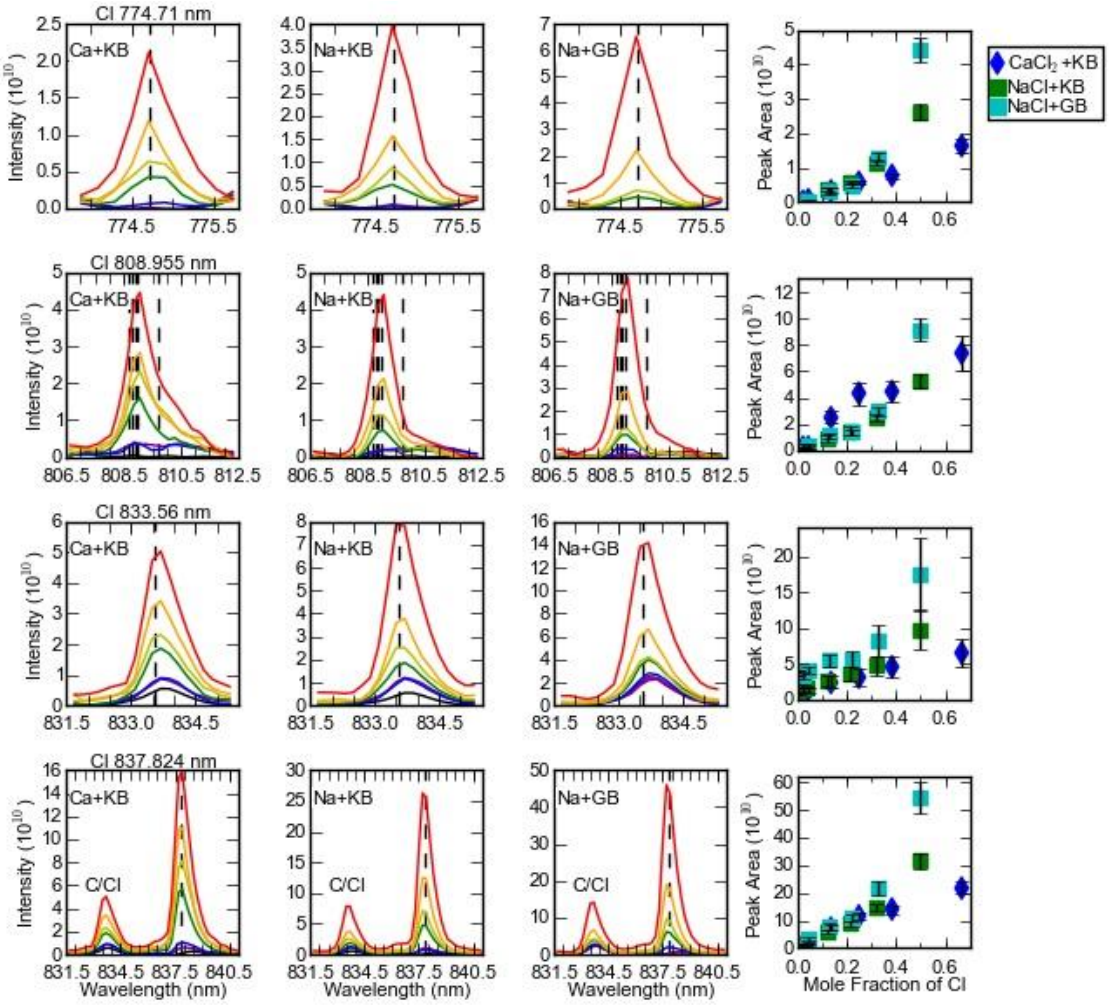

Figure S3. Continued

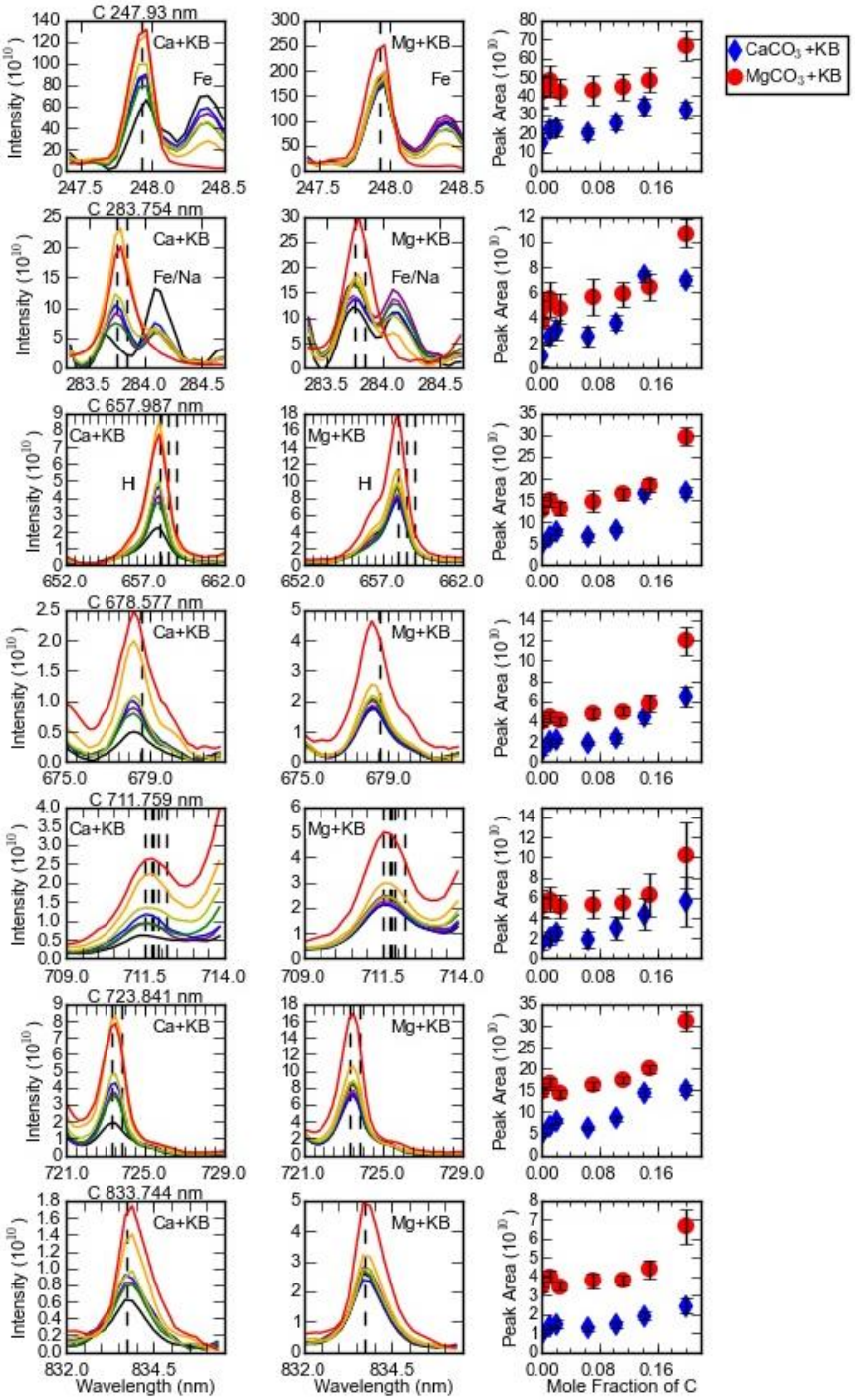

Figure S4. Spectra of C emission lines (denoted by vertical lines) in $CaCO_3$+K1919 (Ca+KB) and $MgCO_3$+K1919 (Mg+KB) mixtures. Colors in the overlain spectra indicate different salt concentrations with pure basalt in black, pure salt in red, and mixtures containing salt mass fractions of 0.05 wt. % (select mixtures only) in magenta, 5 wt. % in purple, 10 wt. % in blue, 30 wt. % in green, 50 wt. % in yellow, and 70 wt. % in orange. Intensity is in units of photons/shot/mm^2/sr/nm. Calibration curves for the corresponding C peaks in $CaCO_3$+K1919 (blue diamonds) and $MgCO_3$+K1919 (red circles) are shown in the rightmost panel. Peak areas are in units of photons/shot/mm^2/sr.

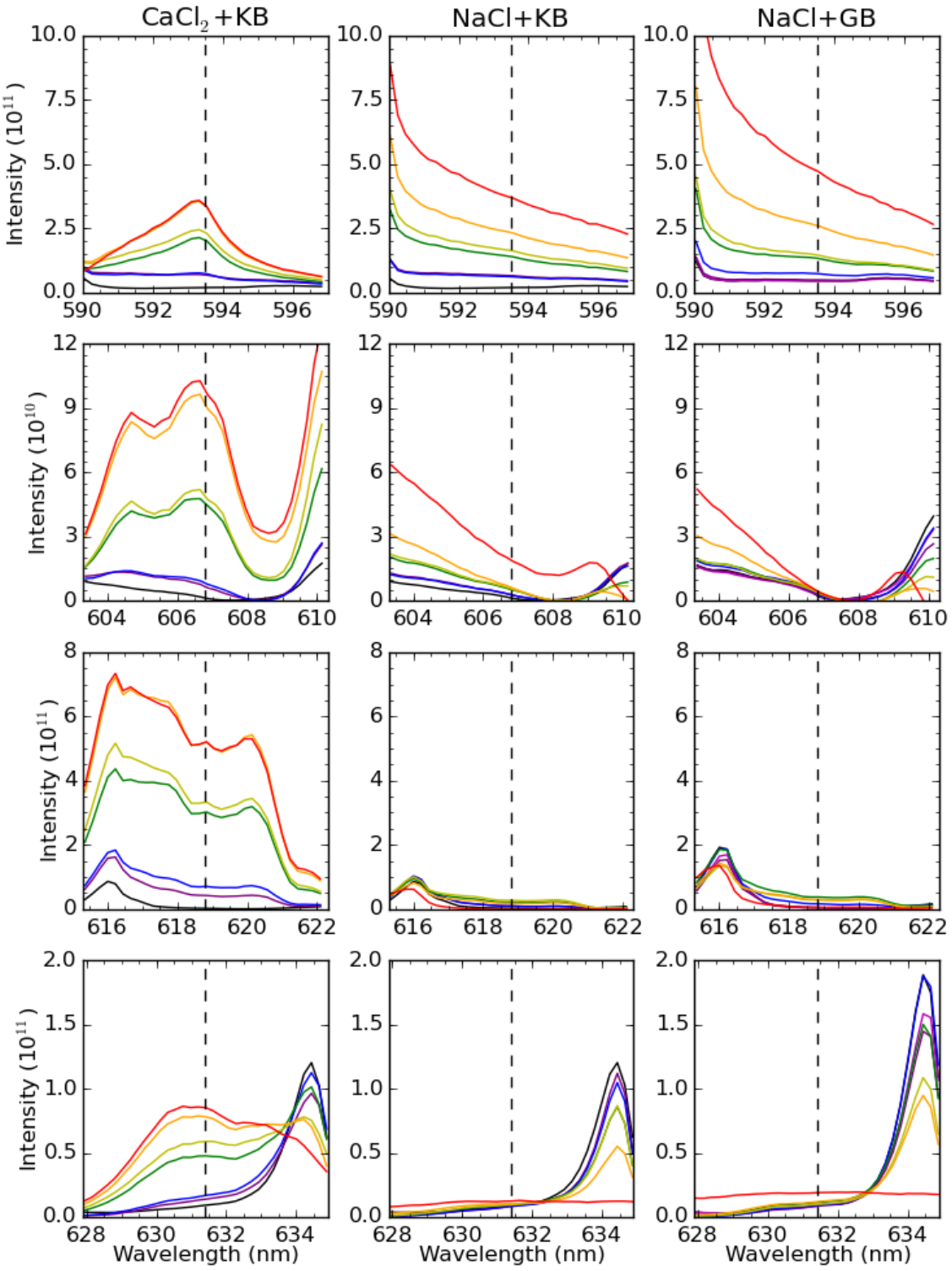

Figure S5. Spectral regions in NaCl+K1919 (Na+KB), $CaCl_2$+K1919 (Ca+KB), and NaCl+GBW07105 (Na+GB) mixtures corresponding to the CaCl lines (denoted by vertical lines) used for the detection of Cl in Martian targets by *Forni et al.* [2015]. Intensity is in units of photons/shot/mm^2/sr/nm.

Table S1. Major element and volatile composition of the endmembers and select mixtures, as independently verified by ActLabs. *Not match predicted values (see Figure S2).

Analyte Symbol	C	S	Cl	SiO2	Al2O3	Fe2O3(T)	MnO	MgO	CaO	Na2O	K2O	TiO2	P2O5	LOI	Total
Unit Symbol	%	%	%	%	%	%	%	%	%	%	%	%	%	%	%
Detection Limit	0.01	0.01	0.01	0.01	0.01	0.01	0.001	0.01	0.01	0.01	0.01	0.001	0.01		0.01
Analysis Method	IR	IR	INAA	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP	FUS-ICP
Basalts															
K1919 - Batch 1	0.01	0.01	0.01	50.65	13.52	12.79	0.166	6.83	11.57	2.28	0.52	2.799	0.28	-0.93	100.50
K1919 - Batch 2	0.02	< 0.01	0.01	50.76	13.66	12.21	0.167	6.96	11.63	2.26	0.51	2.831	0.27	-0.54	100.70
GBW07105	0.06	< 0.01	0.01	43.82	13.33	12.59	0.167	7.45	8.74	3.32	2.24	2.301	1.00	3.19	98.14
Salts and Mixtures - Batch 1															
NaCl (10 wt. %) + K1919	0.02	< 0.01	5.44*	44.47	12.11	10.96	0.150	6.23	10.24	3.47	0.84	2.520	0.24	8.06	99.29
NaCl (50 wt. %) + K1919	0.01	< 0.01	24.80*	24.12	6.57	5.84	0.079	3.37	5.61	4.50	0.29	1.353	0.13	47.28	99.15
NaCl	< 0.01	< 0.01	46.50	< 0.01	< 0.01	0.02	0.002	< 0.01	0.06	43.97	< 0.01	< 0.001	< 0.01	56.77	100.80
CaCO3 (10 wt. %) + K1919	1.16	0.01	0.06	43.97	12.23	10.92	0.152	6.04	16.00	1.96	0.46	2.526	0.25	3.83	98.34
CaCO3 (50 wt. %) + K1919	5.96	< 0.01	0.04	24.28	6.79	6.01	0.100	3.47	34.38	1.10	0.26	1.408	0.14	21.97	99.91
CaCO3	11.5	< 0.01	0.03	0.11	0.01	0.02	0.038	0.22	56.42	< 0.01	< 0.01	0.002	0.01	44.00	100.90
CaSO4 (10 wt. %) + K1919	0.02	1.81	0.06	44.71	12.33	11.00	0.150	6.11	13.94	1.99	0.46	2.521	0.26	4.60	98.07
CaSO4 (50 wt. %) + K1919	0.01	9.31	0.02	24.05	6.75	5.99	0.082	3.35	22.39	1.09	0.26	1.408	0.15	19.96	85.47
CaSO4	0.02	17.70	0.01	0.19	0.09	0.03	0.002	0.04	33.37	< 0.01	< 0.01	0.003	0.01	21.06	54.79
CaCl2 (10 wt. %) + K1919	0.04	0.02	4.89	42.79	11.86	10.63	0.144	5.80	14.32	1.92	0.44	2.431	0.24	9.36	99.94
CaCl2 (50 wt. %) + K1919	0.11	0.07	24.40	22.51	6.44	5.40	0.076	3.13	27.45	1.07	0.25	1.317	0.13	31.79	99.57
CaCl2	0.10	0.10	41.40	0.08	0.02	0.02	0.002	0.03	42.04	< 0.01	< 0.01	0.001	< 0.01	52.70	94.90
Salts and Mixtures - Batch 2															
MgCO3 (10 wt. %) + K1919	1.30	< 0.01	0.02	45.39	12.11	10.75	0.149	8.30	13.17	2.08	0.49	2.532	0.28	3.99	99.24
MgCO3 (50 wt. %) + K1919	6.30	0.01	< 0.01	25.73	6.88	6.11	0.086	13.77	21.53	1.14	0.28	1.436	0.15	22.51	99.62
MgCO3	12.40	< 0.01	< 0.01	1.17	0.29	0.15	0.007	20.71	30.29	0.02	0.04	0.037	0.02	45.69	98.43
MgSO4 (10 wt. %) + K1919	0.02	2.69	0.02	44.20	11.95	10.78	0.147	9.39	10.17	2.00	0.46	2.499	0.25	7.28	99.13
MgSO4 (50 wt. %) + K1919	< 0.01	13.10	< 0.01	24.77	6.74	6.14	0.085	19.80	5.68	1.12	0.26	1.468	0.13	32.40	98.60
MgSO4	< 0.01	26.20	< 0.01	0.09	0.02	0.03	0.004	33.33	0.07	0.01	< 0.01	0.003	< 0.01	47.32	80.89
Fe2(SO4)3 (10 wt. %) + K1919	0.02	1.84	< 0.01	45.11	12.31	13.70	0.159	6.27	10.41	2.06	0.47	2.578	0.28	6.76	100.10
Fe2(SO4)3 (50 wt. %) + K1919	0.02	9.06	< 0.01	24.78	6.64	19.95	0.126	3.81	5.68	1.12	0.26	1.534	0.13	35.00	99.05
Fe2(SO4)3	0.04	18.40	< 0.01	0.19	0.06	28.26	0.088	0.90	0.10	0.02	< 0.01	0.202	< 0.01	70.01	99.84
Na2SO4 (10 wt. %) + K1919	0.02	2.34	0.02	45.58	12.37	11.13	0.151	6.23	10.18	6.49	0.47	2.582	0.28	2.89	98.35
Na2SO4 (50 wt. %) + K1919	0.02	11.10	0.05	25.44	6.92	6.50	0.093	3.59	5.89	21.40	0.28	1.474	0.11	0.59	72.29
Na2SO4	0.02	22.10	0.11	0.19	< 0.01	0.03	0.004	< 0.01	0.03	42.68	< 0.01	0.001	< 0.01	0.46	43.39
CaSO4 (10 wt. %) + GBW07105	0.06	1.88	0.02	39.80	12.20	11.32	0.151	6.65	11.31	2.98	2.03	2.108	0.84	8.61	98.00
CaSO4 (50 wt. %) + GBW07105	0.05	9.42	0.01	20.99	6.54	6.43	0.082	3.69	19.98	1.62	1.08	1.129	0.45	18.53	80.51
CaSO4	0.01	18.40	< 0.01	0.21	0.08	0.02	0.002	0.05	33.87	< 0.01	< 0.01	0.002	< 0.01	21.12	55.37
NaCl (10 wt. %) + GBW07105	0.07	0.03	6.75	39.73	12.31	11.75	0.160	6.95	7.95	7.21	2.08	2.143	0.90	9.19	100.40
NaCl (50 wt. %) + GBW07105	0.04	0.09	27.00	21.44	6.70	6.65	0.091	3.83	4.43	25.06	1.13	1.178	0.45	28.43	99.38
NaCl	< 0.01	0.07	47.40	< 0.01	< 0.01	0.02	0.004	< 0.01	0.07	46.70	< 0.01	0.001	< 0.01	54.09	100.90

Table S2. Identification labels and mixture compositions used for samples from this work included as supplementary data. Bold identification labels indicate samples also included in the database compiled by *Clegg et al.* [2017]. Mixtures 1-5 were shot at a laser-to-sample distance of 1.6 m and mixtures 7-14 were shot at a laser-to-sample distance of 3.0 m.

Label	Wt. % Salt	Salt	Wt. % Basalt	Basalt
Mix1A	5	NaCl	95	K1919
Mix1B	10	NaCl	90	K1919
Mix1C	30	NaCl	70	K1919
Mix1D	50	NaCl	50	K1919
Mix1E	70	NaCl	30	K1919
Mix1O	100	NaCl		
Mix2A	5	CaCO3	95	K1919
Mix2B	10	CaCO3	90	K1919
Mix2C	30	CaCO3	70	K1919
Mix2D	50	CaCO3	50	K1919
Mix2E	70	CaCO3	30	K1919
Mix2O	100	CaCO3		
Mix3A	5	Gypsum	95	K1919
Mix3B	10	Gypsum	90	K1919
Mix3C	30	Gypsum	70	K1919
Mix3D	50	Gypsum	50	K1919
Mix3E	70	Gypsum	30	K1919
Mix3O	100	Gypsum		
Mix5A	5	CaCl2	95	K1919
Mix5B	10	CaCl2	90	K1919
Mix5C	30	CaCl2	70	K1919
Mix5D	50	CaCl2	50	K1919
Mix5E	70	CaCl2	30	K1919
Mix5O	100	CaCl2		
Mix7AA	0.5	MgCO3	99.5	K1919
Mix7A	5	MgCO3	95	K1919
Mix7B	10	MgCO3	90	K1919
Mix7C	30	MgCO3	70	K1919
Mix7D	50	MgCO3	50	K1919
Mix7E	70	MgCO3	30	K1919
Mix7O	100	MgCO3		
Mix8AA	0.5	MgSO4	99.5	K1919
Mix8A	5	MgSO4	95	K1919
Mix8B	10	MgSO4	90	K1919
Mix8C	30	MgSO4	70	K1919
Mix8D	50	MgSO4	50	K1919
Mix8E	70	MgSO4	30	K1919
Mix8O	100	MgSO4		
Mix10AA	0.5	Fe2(SO4)3	99.5	K1919
Mix10A	5	Fe2(SO4)3	95	K1919
Mix10B	10	Fe2(SO4)3	90	K1919
Mix10C	30	Fe2(SO4)3	70	K1919
Mix10D	50	Fe2(SO4)3	50	K1919
Mix10E	70	Fe2(SO4)3	30	K1919
Mix10O	100	Fe2(SO4)3		
Mix11AA	0.5	Na2(SO4)	99.5	K1919

Mix11A	5	Na2(SO4)	95	K1919
Mix11B	10	Na2(SO4)	90	K1919
Mix11C	30	Na2(SO4)	70	K1919
Mix11D	50	Na2(SO4)	50	K1919
Mix11E	70	Na2(SO4)	30	K1919
Mix11O	100	Na2(SO4)		
Mix13AA	0.5	Gypsum	99.5	GBW07105
Mix13A	5	Gypsum	95	GBW07105
Mix13B	10	Gypsum	90	GBW07105
Mix13C	30	Gypsum	70	GBW07105
Mix13D	50	Gypsum	50	GBW07105
Mix13E	70	Gypsum	30	GBW07105
Mix13O	100	Gypsum		
Mix14AA	0.5	NaCl	99.5	GBW07105
Mix14A	5	NaCl	95	GBW07105
Mix14B	10	NaCl	90	GBW07105
Mix14C	30	NaCl	70	GBW07105
Mix14D	50	NaCl	50	GBW07105
Mix14E	70	NaCl	30	GBW07105
Mix14O	100	NaCl		

Supporting Data Files

"Raw" data, collected from the instrument with no processing applied, and "minimally-processed" data, results of the data-processing steps described in section 2.2 of the main text, are included. Data are sorted into directories by the sample name. File names indicate when the measurement was taken: the month and day, a time clock value representing the order in which data were collected, followed by the year. Raw data files end in "spect.TXT" and consist of 29 lines of header information, followed by 50 columns of data representing the spectra in counts collected at each laser shot. Raw data are listed in order of detector: VNIR, VIO, UV. Files are included for each of the sample locations shot and 1-2 "dark" background spectra collected (see section 2.2). Minimally-processed data files end in "minproc.csv" and consist of 2 lines of header information, followed by 51 columns of data where the first column provides the wavelength in nm and remaining columns provide the intensity in photons/shot/mm^2/sr/nm collected at each laser shot. Files are included for each of the sample locations shot.

Also included is a text file, "Calibration_curve_values.txt", containing the peak area values in photons/shot/mm^2/sr for measured compositions of each mixture (using labels from Table S2) and elemental line as shown in Figures 5, S3, and S4. The first line of the text file provides a key to all the values listed.